

# Speciation of Rhenium in Chloride Melts: Spectroscopic and Electrochemical Study

Danil A. Danilov<sup>a</sup>, Vladimir A. Volkovich<sup>a</sup>, Boris D. Vasin<sup>a</sup>, Denis E. Aleksandrov<sup>a</sup>, Ilya B. Polovov<sup>a</sup>, and Trevor R. Griffiths<sup>b</sup>

<sup>a</sup> Department of Rare Metals, Ural State Technical University, 620002 Ekaterinburg, Russia

<sup>b</sup> Redston Trevor Consulting Limited, Leeds, LS17 8RF, United Kingdom

Reprint requests to Dr. V. A. V.; E-mail: volkovich@dpt.ustu.ru

Z. Naturforsch. **63a**, 371 – 376 (2008); received December 12, 2006

*Presented at the EUCHEM Conference on Molten Salts and Ionic Liquids, Hammamet, Tunisia, September 16–22, 2006.*

Speciation of rhenium in high-temperature alkali chloride-based melts was studied using electronic absorption and IR spectroscopy of molten salts and diffuse reflectance spectroscopy of quenched melts. Rhenium was added to the melts by anodic dissolution of the metal (at anodic current densities of 0.005–0.05 A/cm<sup>2</sup>), by reacting Re and ReO<sub>2</sub> with Cl<sub>2</sub> and HCl, and by dissolving K<sub>2</sub>[ReCl<sub>6</sub>]. The melts included 3LiCl-2KCl and NaCl-2CsCl eutectics, an NaCl-KCl equimolar mixture, and pure NaCl, KCl and CsCl between 450 and 850 °C. Rhenium was present in the melts as Re(IV) hexachloro-ions, [ReCl<sub>6</sub>]<sup>2-</sup>; no evidence of species containing rhenium in oxidation states below four was obtained. The kinetics of [ReCl<sub>6</sub>]<sup>2-</sup> disproportionation in molten alkali chlorides were investigated, and the IR spectra of [ReO<sub>4</sub>]<sup>-</sup> ions in molten CsCl-CsI and CsI were measured for the first time.

**Key words:** Rhenium; Rhenium Chlorides; Chloride Melts; Electronic Absorption Spectroscopy.

## 1. Introduction

Electrolytic reduction of rhenium from chloride melts is a prospective method for obtaining high-purity metal. Knowing the speciation of rhenium and the stability of its ions in such media is important for optimizing the methods of preparing rhenium-containing melts and processes of rhenium electrowinning. Only a few works were devoted to investigating the behaviour of rhenium in alkali halide melts and other ionic media.

Electronic absorption spectra of solutions of K<sub>2</sub>[ReCl<sub>6</sub>] have been measured in molten 3LiCl-2KCl eutectic and dimethyl sulfone between 135 and 600 °C [1]. The behaviour of Re(III) chloride species, Re<sub>3</sub>Cl<sub>9</sub>, [Re<sub>3</sub>Cl<sub>12</sub>]<sup>3-</sup> and [Re<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup>, in the same melts has also been investigated [2]. In a 3LiCl-2KCl melt Re(III) disproportionates to Re(0) and [ReCl<sub>6</sub>]<sup>2-</sup>. Raman spectroscopy was employed to study the reaction of rhenium metal with molten lithium perchlorate at 250–300 °C [3]; perrhenate was the only product formed. Bailey and Nobile [4] conducted an electrochemical study of rhenium in molten 3LiCl-2KCl eutectic at 450–550 °C. They found that

anodic dissolution of rhenium results in a mixture of Re(III) and Re(IV) chloride complexes; Re(III) ions disproportionate to Re(0) and Re(IV). Upon dissolving K<sub>2</sub>[ReCl<sub>6</sub>] in the same melt, the authors [4] noted partial decomposition of this salt to Re metal and volatile ReCl<sub>5</sub>. However, in their opinion, after complete dissolution the decomposition reaction ceased and rhenium(IV) complexes, [ReCl<sub>6</sub>]<sup>2-</sup>, stabilized. Stepanov et al. [5] conducted electrochemical studies of Re in an NaCl-KCl melt and concluded that Re(IV) and Re(V) ions are present in the melt in equilibrium with rhenium metal. Later Stepanov et al. [6] studied the anodic dissolution of rhenium and found that at a current density of 0.4–1.2 A/cm<sup>2</sup> Re dissolves, giving out four electrons; at current densities below 0.15 A/cm<sup>2</sup> the number of electrons falls below four. Electronic absorption spectra of Re(III) and Re(IV) ions ([Re<sub>2</sub>Cl<sub>8</sub>]<sup>2-</sup>, [Re<sub>2</sub>Cl<sub>8</sub>]<sup>3-</sup>, Re<sub>3</sub>Cl<sub>9</sub>, [ReCl<sub>6</sub>]<sup>2-</sup>, [Re<sub>2</sub>Cl<sub>9</sub>]<sup>-</sup>, [Re<sub>2</sub>Cl<sub>9</sub>]<sup>2-</sup>) were also measured in low-temperature ionic melts based on 1-methyl-3-ethylimidazolium chloroaluminate and AlCl<sub>3</sub>-NaCl [7–9]. On the basis of electrochemical studies of the rhenium behaviour in fused alkali chlo-

rides Kuznetsov [10] concluded that only Re(III) ions are present in molten NaCl, and only Re(IV) in molten KCl and CsCl. This was explained by the effect of the outer sphere cations onto rhenium chloro-complexes due to differences in the ionic potentials of alkali metal cations. Kuznetsov [10] also suggested that disproportionation of Re(III) and Re(IV) ions observed in earlier works results from the interaction of rhenium chlorides with silica, leading to the formation of higher oxidation state rhenium oxychlorides and Re metal. Volkovich *et al.* [11] employed high-temperature spectroscopy to study reactions of Re, ReO<sub>2</sub> and ReO<sub>3</sub> with Cl<sub>2</sub> and HCl in various alkali metal chlorides between 450 and 720 °C. They found that Re(0) reacts with Cl<sub>2</sub> in an NaCl-2CsCl eutectic forming only Re(IV) complex ions. Spectra measured during chlorination of Re in 3LiCl-2KCl and NaCl-KCl melts in addition to [ReCl<sub>6</sub>]<sup>2-</sup> bands contained some additional absorption bands. Reaction of rhenium oxides with Cl<sub>2</sub> or HCl in an NaCl-2CsCl melt results in the formation of Re(IV) ions.

In the present work electronic absorption and IR spectroscopy of molten salts and diffuse reflectance spectroscopy of quenched melts was used to study the speciation of rhenium in molten alkali metal chlorides and their mixtures. Rhenium was added to the melts by anodic dissolution of the metal, by reacting Re and ReO<sub>2</sub> with Cl<sub>2</sub> and HCl, and by dissolving K<sub>2</sub>[ReCl<sub>6</sub>] and Na[ReO<sub>4</sub>]. The studied melts included 3LiCl-2KCl and NaCl-2CsCl eutectics, an NaCl-KCl equimolar mixture, and pure NaCl, KCl and CsCl between 450 and 850 °C. The kinetics of [ReCl<sub>6</sub>]<sup>2-</sup> decomposition were investigated, and for the first time the IR spectra of [ReO<sub>4</sub>]<sup>-</sup> ions were measured in molten CsI and CsI-CsCl.

## 2. Experimental

Electronic absorption spectra were recorded using a system based on a fibre optics Ocean Optics SD2000 spectrometer and an optical high-temperature furnace [11]. Melts were contained in standard high-temperature 1 cm path length silica optical cells. Spectral data were collected in the 250–1100 nm range. IR emission spectra were registered using a SPECORD M80 spectrophotometer with a special high-temperature optical attachment with a CsI window [12]. A previously described system [13] was used for in situ spectroscopy studies of anodic dissolution. Diffuse reflectance spectra of powdered quenched

melts were measured using a setup described earlier [14]. When required, the experimental spectra were resolved into individual overlapping bands using Peak-Fit version 4.01 software.

The experiments were performed in molten individual NaCl, KCl and CsCl, 3LiCl-2KCl and NaCl-2CsCl eutectics and an NaCl-KCl equimolar mixture. Individual reagent grade alkali metal chlorides were dried for 3 h at 300 °C and then melted. Molten salts were sparged with chlorine and hydrogen chloride for 5 h and then held under vacuum. Mixtures of required compositions were prepared by fusing individual chlorides in vacuo and then subjected to zone recrystallization under vacuum.

Rhenium was added to the melts by anodic dissolution of metal (99.99% purity) at anodic current densities of 0.005–0.05 A/cm<sup>2</sup>, by chlorinating Re and ReO<sub>2</sub> by Cl<sub>2</sub> and HCl bubbled through the melts at a rate of 10–60 cm<sup>3</sup> min<sup>-1</sup>, and by directly dissolving K<sub>2</sub>[ReCl<sub>6</sub>] and Na[ReO<sub>4</sub>]. All the processes (chlorination and dissolution) were followed by in situ spectroscopy measurements. K<sub>2</sub>[ReCl<sub>6</sub>] was prepared from K[ReO<sub>4</sub>] following a standard procedure [15]. Chlorine was generated by electrolysis of molten lead chloride, and HCl by reaction of conc. H<sub>2</sub>SO<sub>4</sub> with NaCl. For anodic dissolution a piece of rhenium (owing to a very positive electrode potential) was suspended on a carbon thread, which also acted as a current conductor. A molybdenum wire dipped in a melt containing PbCl<sub>2</sub>, held in a silica tube separated from the bulk of the melt by a diaphragm, acted as the cathode. For spectroelectrochemical measurements the optical cell also contained a glassy carbon working electrode (*S* = 0.032 cm<sup>2</sup>) and an Ag/AgCl (1 mol% in NaCl-2CsCl) reference electrode. A PI-50-1.1 potentiostat was used for all the electrochemical measurements.

After every experiment samples of the melts (1–2 cm<sup>3</sup>) were sucked into silica capillary tubes, using a syringe, and quickly quenched. The concentration of rhenium in these samples was determined photometrically with thiourea [16].

## 3. Results and Discussion

Re anodic dissolution was studied in 3LiCl-2KCl, NaCl and NaCl-2CsCl melts at 450–850 °C at anodic current densities between 0.005 and 0.05 A/cm<sup>2</sup>. The profiles of the spectral curves in all these melts at all studied temperatures and current densities were qualitatively similar (an example is given in Fig. 1)

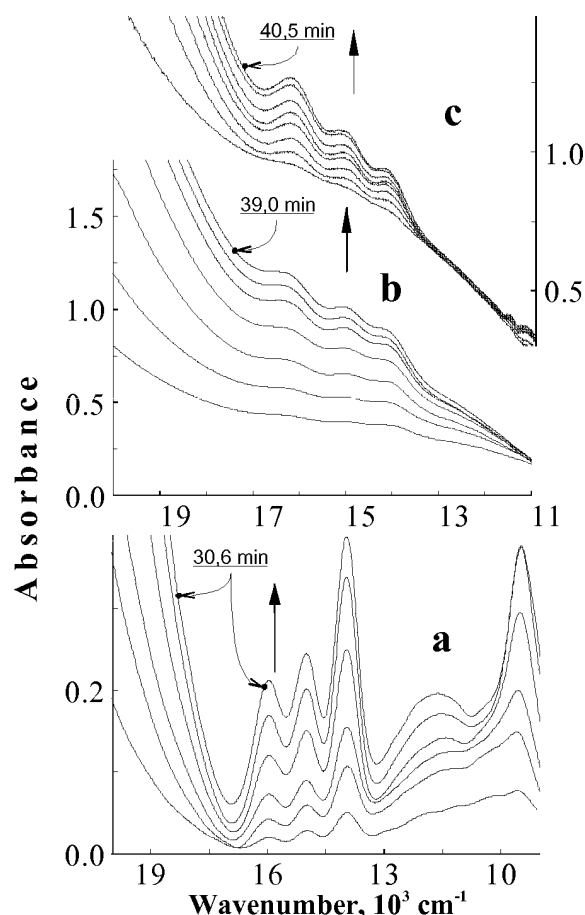


Fig. 1. Electronic absorption spectra recorded during anodic dissolution of Re in molten (a) NaCl-2CsCl at 550 °C, (b) NaCl and (c) NaCl-2CsCl at 850 °C. Final Re concentration in melts was 14, 18 and 1 mmol/l, respectively.

and characteristic of the absorption of rhenium(IV)  $[\text{ReCl}_6]^{2-}$  ions. Observed absorption bands arise from the following spin-forbidden electronic transitions in  $[\text{ReCl}_6]^{2-}$  complex ions:  $^4A_{2g}(\Gamma_8) \rightarrow ^2T_{2g}(\Gamma_8)$  at 15000 and 16000  $\text{cm}^{-1}$ ;  $^4A_{2g}(\Gamma_8) \rightarrow ^2T_{2g}(\Gamma_7)$  at 14000  $\text{cm}^{-1}$ ; and  $^4A_{2g}(\Gamma_8) \rightarrow ^2E_g(\Gamma_8)$  and  $^4A_{2g}(\Gamma_8) \rightarrow ^2T_{1g}(\Gamma_6)$  at 9100–9500  $\text{cm}^{-1}$ . Bands at 15000 and 16000  $\text{cm}^{-1}$  result from the term splitting due to spin-orbit coupling. The nature of the broad band at 11600  $\text{cm}^{-1}$  is not yet clear. More intense bands, originating from the spin-allowed transitions, are situated at higher energies and could not be registered using the present experimental setup. The obtained energy values correspond to literature data [1, 2, 10]. No bands indicating the possible existence of Re(III) ions in NaCl or 3LiCl-2KCl melts were observed. IR spectra

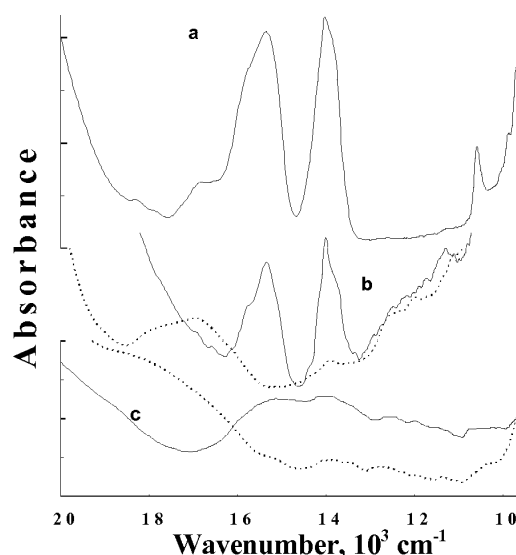


Fig. 2. Diffuse reflectance spectra of (a) pure  $\text{K}_2[\text{ReCl}_6]$ , and green (dashed line) and yellow (solid line) parts of quenched melt samples after anodic dissolution of rhenium in (b) NaCl-2CsCl and (c) NaCl melts.

of quenched melt samples contained the peaks corresponding to the “ $\text{Re}^{\text{IV}}\text{Cl}_6$ ” moiety of  $O_h$  symmetry. There were no bands that could be attributed to per-rhenate, oxychloro- or polynuclear rhenium species.

It was noticed that the colour of quenched melt samples depended on the rate of quenching. Slowly quenched samples were yellow, and their diffuse reflectance spectra included bands at 14000 and 15400  $\text{cm}^{-1}$  corresponding to  $\text{M}_2[\text{ReCl}_6]$  (Fig. 2). Rapidly quenched samples were brownish-green, and their diffuse reflectance spectra contained an additional band around 16700–18200  $\text{cm}^{-1}$ , seen as a shoulder in the experimental spectrum. This band probably corresponds to one of the products of disproportionation of  $[\text{ReCl}_6]^{2-}$ , occurring at sudden melt quenching.

A special series of experiments was performed to study the stability of the  $[\text{ReCl}_6]^{2-}$  complex in chloride melts. Samples of pure  $\text{K}_2\text{ReCl}_6$  were dissolved in selected melts under argon, and the absorption spectra were recorded over time. The Re(IV) concentration in the melts gradually decreased, Fig. 3, and did stabilize as reported by Bailey and Nobile [4]. At the same time a dark-blue compound, presumably  $\text{ReCl}_5$ , was subliming from the melt and condensing in the upper cold part of the cell. Chemical analysis of this compound showed the presence of rhenium, however, the small amount of this sublimate and its hygroscopic nature did not allow to perform more detailed charac-

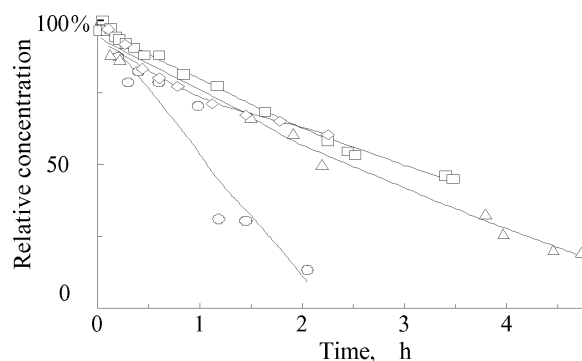
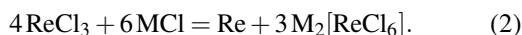
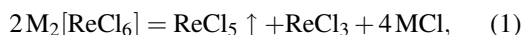


Fig. 3. Decreasing  $[\text{ReCl}_6]^{2-}$  concentration (relative) over time at 750 °C in molten alkali chlorides:  $\square$ , NaCl-KCl;  $\circ$ , 3LiCl-2KCl;  $\triangle$ , NaCl-2CsCl;  $\diamond$ , CsCl.

terization. If the cell was evacuated, the concentration of  $[\text{ReCl}_6]^{2-}$  in the melt rapidly decreased. This fact also supports the assumption that one of the products of  $[\text{ReCl}_6]^{2-}$  decomposition must be volatile. The decomposition most likely proceeds according to the following scheme, proposed by Bailey and Nobile [4]:



With the exception of lithium-containing chloride melts, the cationic composition of the melt did not significantly affect the rate of  $[\text{ReCl}_6]^{2-}$  decomposition (Fig. 3). Increasing temperature resulted in increased rates of decomposition in all studied systems. It is quite likely that formed rhenium pentachloride,  $\text{ReCl}_5$ , partially dissolves in the melt, and Re(V) chloride ions,  $[\text{ReCl}_6]^-$ , absorb in the UV region of the spectrum. However, since  $[\text{ReCl}_6]^{2-}$  ions strongly absorb above  $19000\text{ cm}^{-1}$  the effect of Re(V) onto the profile of the spectral curve cannot be observed under the studied conditions.

A series of spectroelectrochemical experiments in 3LiCl-2KCl and NaCl-KCl melts was performed at 550 and 750 °C, respectively, to check Kuznetsov's [10] suggestion about the possibility of stabilizing Re(III) ions in alkali chloride melts with small cations. Rhenium metal was anodically dissolved in these melts, forming  $[\text{ReCl}_6]^{2-}$ , and cyclic voltammograms were then measured to determine suitable reduction potentials. An example of a cyclic voltammogram is shown in Fig. 4; it exhibits two anodic and two cathodic waves and agrees with the data reported by Kuznetsov [10] for 2NaCl-3KCl, KCl and CsCl melts. According to Kuznetsov [10] only one cathodic and

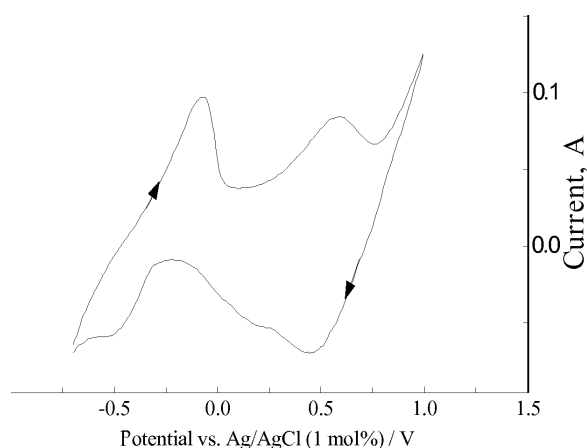


Fig. 4. Cyclic voltammogram of  $[\text{ReCl}_6]^{2-}$  containing NaCl-KCl-based melt at 750 °C prepared by anodic dissolution of Re metal. Working electrode, glassy carbon ( $S = 0.032\text{ cm}^2$ ); reference electrode, Ag/AgCl (1 mol% in NaCl-2CsCl); counter electrode, molybdenum wire in NaCl-2CsCl+ $\text{PbCl}_2$ ; rest potential, +0.82 V; scan rate, 0.1 V/s; initial Re content, 0.8 wt%.

one anodic peak (corresponding to the Re(III)/Re(0) redox couple) should be expected in 3LiCl-2KCl and NaCl-KCl melts; but in both these melts we observed two reduction and two oxidation waves.

Assuming that the reduction peaks in the cyclic voltammograms, Fig. 4, correspond to  $\text{Re(IV)} \rightarrow \text{Re(III)}$  and  $\text{Re(III)} \rightarrow \text{Re(0)}$  reactions, the potentiostatic reduction of rhenium-containing melts was conducted at potentials ranging from +0.2 to -0.1 V. During the reduction the concentration of Re(IV) in the melt gradually decreased, but no new peaks in the spectra, that could be attributed to lower oxidation state rhenium ions, appeared. At the end of the reduction (taking 1.5–3.5 h) the melt contained a fine precipitate of metallic rhenium, and the content of rhenium in the melt was low (0.007–0.065 wt% in various experiments). It seems that Re(III) ions can only be formed near the electrode surface during the cathodic reduction of Re(IV) ions, and can be detected by electrochemical methods, but cannot be stabilized in the bulk of the melt in spectroscopically detectable amounts, at least when using silica optical cells.

The reaction of metallic rhenium with chlorine in chloride melts resulted in the formation of  $[\text{ReCl}_6]^{2-}$  ions (Fig. 5). Studying this reaction in various molten alkali chlorides showed that the cationic composition of the melt affects the rate of the chlorination (Table 1). Compact rhenium (used as a piece with a total surface area around  $0.6\text{ cm}^2$ ) or Re metal powder

Table 1. Chlorination of Re and ReO<sub>2</sub> in alkali chloride melts.

Melt	Compound	<i>T</i> , °C	Chlorinating agent	Time of chlorination, h	Max. conc. of Re in melt, mmol/l
NaCl-2CsCl	Re (powder)	750	Cl <sub>2</sub>	4.8	38.4
NaCl-KCl	Re (powder)	800	Cl <sub>2</sub>	0.9	6.5
CsCl	Re (powder)	800	Cl <sub>2</sub>	1.1	10.4
NaCl-KCl	Re (piece)	850	Cl <sub>2</sub>	3.0	not found
NaCl-2CsCl	Re (piece)	850	Cl <sub>2</sub>	1.2	7.8
NaCl-2CsCl	ReO <sub>2</sub>	650	Cl <sub>2</sub>	1.7	20.7
NaCl-KCl	ReO <sub>2</sub>	750	Cl <sub>2</sub>	0.9	3.4
3LiCl-2KCl	ReO <sub>2</sub>	500	HCl	6.7	not found
NaCl-KCl	ReO <sub>2</sub>	750	HCl	3.5	not found
NaCl-2CsCl	ReO <sub>2</sub>	600	HCl	4.1	24.8
NaCl-2CsCl	ReO <sub>2</sub>	800	HCl	3.5	not found
KCl	ReO <sub>2</sub>	850	HCl	4.7	not found

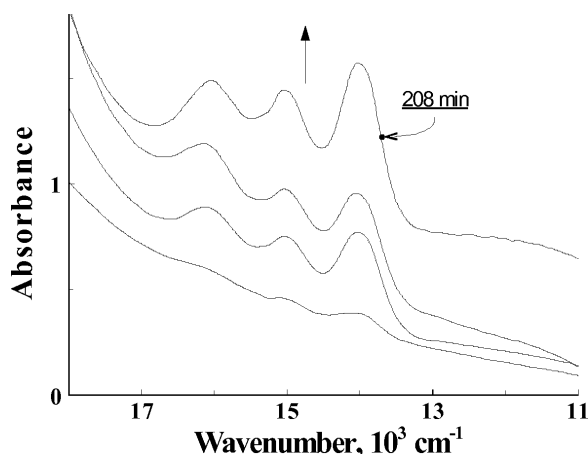
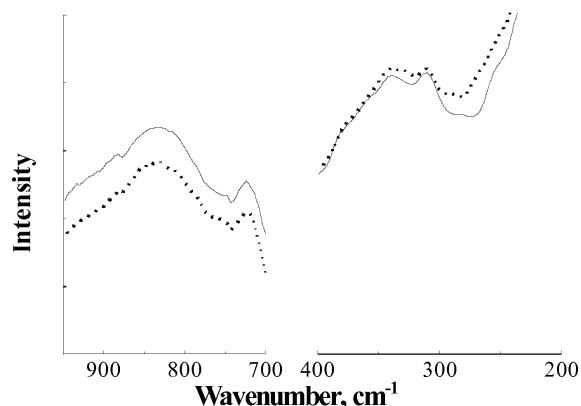


Fig. 5. Electronic absorption spectra recorded during reaction of metallic rhenium with chlorine in an NaCl-2CsCl melt at 750 °C. Final Re concentration in the melt was 0.04 mol/l.

(20 mg per 1 cm<sup>3</sup> of the melt) were used for this study. Data in the table show that the rate of chlorination increases with increasing radius of alkali metal cations, due to the increasing solubility of chlorine.

The reaction of rhenium dioxide with Cl<sub>2</sub> or HCl in alkali chloride melts (approx. 15 mg ReO<sub>2</sub> per 1 cm<sup>3</sup> of the melt) also results mainly in the formation of [ReCl<sub>6</sub>]<sup>2-</sup> complex ions in the melt. When ReO<sub>2</sub> reacted with chlorine, the rate of accumulation of [ReCl<sub>6</sub>]<sup>2-</sup> in the melt was 6 · 10<sup>-8</sup> mol/min in NaCl-KCl at 750 °C and 2.1 · 10<sup>-7</sup> mol/min in NaCl-2CsCl at 650 °C. The rate of the reaction of ReO<sub>2</sub> with HCl was somewhat lower. After several hours of reaction the concentration of [ReCl<sub>6</sub>]<sup>2-</sup> in 3LiCl-2KCl at 500 °C, NaCl-KCl at 750 °C, NaCl-2CsCl at 800 °C and KCl at 850 °C did not reach spectroscopically detectable levels. In the NaCl-2CsCl eutectic at 600 °C the rate of accumulation of [ReCl<sub>6</sub>]<sup>2-</sup> was 10<sup>-7</sup> mol/min.

Fig. 6. IR emission spectra of [ReO<sub>4</sub>]<sup>-</sup> solution in molten CsI (solid line) and 85%CsI-15%CsCl (dotted line) at 600 °C.

Another rhenium species stable in high-temperature melts is perrhenate, [ReO<sub>4</sub>]<sup>-</sup>. This species, however, does not absorb in the visible region (only a low-energy edge of the charge transfer spectrum lying above 31200 cm<sup>-1</sup> was observed in NaCl-2CsCl melt), and for its detection IR spectroscopy of molten salts had to be employed. Since alkali chloride melts absorb strongly below 500–300 cm<sup>-1</sup> we used another solvent, CsI, transparent in that region. The IR spectra of Na[ReO<sub>4</sub>] dissolved in molten CsI and CsI-CsCl (15%) at 600 °C are shown in Figure 6. Two bands in the spectra were attributed to vibrations in the [ReO<sub>4</sub>]<sup>-</sup> ion of *T<sub>d</sub>* symmetry, degenerated stretching vibration *v<sub>d</sub>*(Re-O) at 835 cm<sup>-1</sup> and degenerated bending vibration *δ<sub>d</sub>*(O-Re-O) at 330–315 cm<sup>-1</sup>. The nature of the band around 725 cm<sup>-1</sup> is not clear.

#### 4. Conclusions

The conducted spectroscopy studies showed that [ReCl<sub>6</sub>]<sup>2-</sup> and [ReO<sub>4</sub>]<sup>-</sup> ions are stable in high-tem-

perature chloride melts. Anodic dissolution of Re independently of the cationic composition of the melt and anodic current densities (in the range of 0.005–0.05 A/cm<sup>2</sup>) resulted in the formation of Re(IV) ions, [ReCl<sub>6</sub>]<sup>2−</sup>. No absorption bands that could be attributed to Re(III) ions were observed in the spectra

measured during anodic dissolution. Chlorination of metallic Re or ReO<sub>2</sub> by Cl<sub>2</sub> or HCl and dissolution of K<sub>2</sub>[ReCl<sub>6</sub>] in the melts of various cationic compositions and in a wide temperature range led to the formation of Re(IV) ions in the melt. [ReCl<sub>6</sub>]<sup>2−</sup> slowly disproportionated forming Re metal and volatile ReCl<sub>5</sub>.

- [1] R. A. Bailey and J. A. McIntyre, *Inorg. Chem.* **5**, 964 (1966).
- [2] R. A. Bailey and J. A. McIntyre, *Inorg. Chem.* **5**, 1940 (1966).
- [3] D. Cohen, S. Fried, and H. Selig, *J. Inorg. Nucl. Chem.* **33**, 2687 (1971).
- [4] R. A. Bailey and A. A. Nobile, *Electrochim. Acta* **17**, 1139 (1972).
- [5] A. D. Stepanov, S. N. Shkolnikov, A. M. Ezrokhina, and U. V. Boboshkin, *Izv. Vuzov, Tsvet. Met.* **5**, 65 (1985).
- [6] A. D. Stepanov, M. M. Vetyukov, and S. N. Shkolnikov, in: *V. Urals Conference on High Temperature Physics, Chemistry and Electrochemistry*, Vol. 1, Sverdlovsk, 1989, p. 230.
- [7] S. K. D. Strubinger, I.-W. Sun, W. E. Cleland, Jr., and C. L. Hussey, *Inorg. Chem.* **29**, 993 (1990).
- [8] S. K. D. Strubinger, I.-W. Sun, W. E. Cleland, Jr., and C. L. Hussey, *Inorg. Chem.* **29**, 4246 (1990).
- [9] S. K. D. Strubinger, W. E. Cleland, and C. L. Hussey, *Inorg. Chem.* **30**, 4276 (1991).
- [10] S. A. Kuznetsov, *Elektrokhimiya* **30**, 1462 (1994).
- [11] V. A. Volkovich, I. May, J. M. Charnock, and B. Lewin, *Phys. Chem. Chem. Phys.* **4**, 5753 (2002).
- [12] A. A. Khokhryakov, *Electronic and Infrared Spectra of Oxyhalide Melts: Dilute Solutions*, DSc Thesis, Institute of Metallurgy, Ekaterinburg, Russia 1999 (in Russian).
- [13] I. B. Polovov, V. A. Volkovich, S. A. Shipulin, S. V. Maslov, A. A. Khokhryakov, B. D. Vasin, T. R. Griffiths, and R. C. Thied, *J. Mol. Liquids* **105**, 105 (2003).
- [14] T. R. Griffiths, V. A. Volkovich, D. J. Fray, and M. Fields, *Dyes and Pigments* **39**, 139 (1998).
- [15] C. L. Rulfs and R. S. Meyer, *J. Am. Chem. Soc.* **77**, 4505 (1955).
- [16] A. I. Lazarev, *Organic Reagents in Analysis of Metals*, Metallurgiya, Moscow 1980, p. 232 (in Russian).